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SOUND VELOCITY AND INTER-MOLECULAR ACTION IN LIQUIDS

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ABSTRACT. Attempt is made to explain and discuss Parthasarathy's empirical rules between sound velocity and constitution of pure organic liquids, On the basis of the theory of intermolecular attractive forces, it is shown how cohesion and sound velocity depend upon the molecular structure of liquids. Some further rules, especially between diamagnetic susceptibility and velocity are introduced. Effect of association on compressibility and factors giving rise to cohesion and viscosity are also discussed.

INTRODUCTION

Parthasarathy (1937) has given some interesting rules relating sound velocity in liquids and their chemical constitution. They are all empirical rules. Attempt is made in the following to discuss and explain the rules on the basis of the molecular structure and theory of intermolecular forces. Some other rules are also introduced and discussed.

The rules given by Parthasarathy may be summarised as below, along with examples given by him :

(1) Aromatic compounds have usually higher velocities than the aliphatics. Benzene has velocity 1310 m/s and ethyl alcohol 1207.

(2) Among aromatic compounds, the ortho substituents have usually the greatest velocities and para the least. The effect, however, is small and may be swamped out by some opposite considerations.

Examples :—

Liquid	Velocity Meters/Sec.	Compressibility $\beta_{adiabatic} \times 10^6$	Temp. °C
o-dichlorobenzene	1246	49·7	28.c
m-dichlorobenzene	1232	51·2	28°
o-xolene	1352	62.4	22°
m-xylene	1328	65.9	22°
p-xylene	1339	65 9	22°

(3) For paraffins, aliphatic alcohols and ketones the velocity increases as chain length increases.

Liquid	V	Compressibility $\beta \times 10^6$	Temperature C°
Hexane	1113	122 7	23
Heptane	1165	108.1	23
Ethyl Alcohol	1207	87 3	23
Propyl Alcohol	1234	81.3	23
Acetone	1203	87.4	22.5
Diethyl ketone	1314	71 2	24

(4) As the chain length of ester or ether in increased velocity decreases.

Liquid	V	$\beta \times 10^6$	Temp. C°
Methyl acetate	1211	73 5	24
Ethyl acetate	1187	79 0	23.5
Propyl acetate	1182	80.3	26
Amyl acetate	1168	83.0	26

(5) Viscous liquid have greater velocities :—Viscosity and velocity increase in the direction ethyl alcohol, ethylene glycol and glycerine. Compressibility decreases in the same order.

(6) Liquids whose molecules have dipole moments show enhanced velocities.

	V	$\beta \times 10^6$	Temp C°
Benzene	1310	66.8	23
Nitrobenzene	1455	37 6	28
Cyclonexane	1257	81.9	23
Cyclonaxanone	1441	50.8	23.5

Other examples are paraffins and their corresponding alcohols

(7) Introduction of a heavier atom into the molecule brings down the velocity. Also the introduction of a greater number of the same heavy atom tends to lower the sound velocity.

For example see p. 56.

(8) Usually the introduction of a double bond favours lowering of sound velocity.

Liquid		$\beta \times 10^6$	Temp. C°
(a) Acetylene dichloride $CHCl : CHCl$	1045	75.4	25
Tetra chloroethane $Cl_2HC.CHCl_2$	1155	48.6	28
(b) Tetra-chloroethane	1155	48.6	28
Tetra-chloroethylene $Cl_2C : CCl_2$	1027	58.4	28

(9) Among isomers, if isomerism is not of the optical kind, there is difference in sound velocity. The xylenes, α and β picolines, butyl and isobutyl alcohol show such difference. But the optical isomers, the d and l pinens possess identical velocity.

DISCUSSION AND EXPLANATION OF RESULTS

1. Now the fundamental factor with regard to the structure of liquids is not the velocity of sound waves in them but their compressibility (pointed out by Bergmann also), adiabatic or isothermal, given by

$$V = \frac{1}{\sqrt{d\beta}},$$

where V is velocity, d density and β the adiabatic compressibility.

The author (Parshad, 1941) has shown previously how to link up compressibility with molecular forces and only big points may be presented again.

Among molecules three kinds of forces have been recognised. (1) General forces, or dispersion or London forces.

They act among all kinds of molecules. The simplified, and approximate, formula as given by London is

$$U = -\frac{3}{4} \cdot \frac{\alpha^2 V}{R^6}, \qquad \ldots \quad (1)$$

where α is polarisability of one molecule,
V is ionisation or excitation potential,
R is distance between the two interacting molecules.

2. Orientation forces or keesom forces.

These forces, as first shown by Keesom (1916), act between dipoles only. At moderate temperatures the energy of interaction U between two molecules is given by

$$U = -\frac{2}{3} \cdot \frac{\mu_1^2 \mu_2^2}{KTR^6}, \qquad \ldots \quad (2)$$

where μ_1 and μ_2 are the dipole moments of the interacting dipoles and R is the distance between them.

Other symbols have their usual meaning.

3. Induction forces or Debye forces.

It was shown first by Debye (1921) that there can be attraction between a polar molecule and a non-polar molecule in virtue of the non-polar molecule being induced upon by the polar, prior to attraction. These forces are the least important but are independent of temperature.

The expression for the interaction energy is

$$U = -\frac{\mu_1^2\alpha_2 + \mu_2^2\alpha_1}{R^6}, \qquad \ldots (3)$$

where α_1, α_2 are the polarisabilities of the molecules. Other symbols have the meanings given above.

Apart from these attractive forces functioning in molecular organic liquids under consideration, there are also found to be repulsive forces coming into importance at very small distances, and in fact varying inversely as 9th or 10th power of the distance. Their source was not clear on classical ideas, but now has been cleared up on quantum mechanical considerations. Generally then we may have interaction energy E between two molecules where E is given by

$$E = \frac{C_r}{R^n} - \frac{C_a}{R^6},$$

where n is of order 9 to 12, R is intermolecular distance, C_r is constant for repulsive fields and C_a for attractive fields.

The molecules would be in positions of minimum free energy or approximately minimum potential energy. Now it is easy to visualise that the greater the attractive constant C_a, the nearer will the molecules be to each other till the separating influence of repulsive fields and temperatures bring them to a stop. At that the cohesive energy will be the greatest.

Note.—Minimum potential energy corresponds to greatest cohesive energy since the latter is of negative sign.

Now it can also be seen that with cohesive energy great, compressibility will be small. The nearer are the molecules to each other, the greater will be the change in energy for each small progressive displacement as it will be a greater proportion of the existing intermolecular distance the smaller the latter distance already is. In other words the smaller the distance between molecules, the greater the rate of change of energy, and hence lower the compressibility. This idea can be put as below :

$E \propto \frac{1}{R}$, where the power of R is not mentioned

$$\frac{\partial^2 E}{\partial R^2} \propto \frac{1}{R^3} \propto \frac{1}{R}.$$

$\frac{\partial^2 E}{\partial R^2}$ is of course related to modulus of elasticity (neglecting the temperature effect) and inverse to compressibility.

Hence

$$\text{Compressibility} \propto \frac{1}{E} \propto \frac{1}{C_a}$$

The exact evaluation of compressibility, considering the entropy and temperature, involves difficulties and has not been done satisfactorily to date. The calculation is however particularly easy, considering only two molecules and their displacement in their mutual direction, neglecting the temperature effect, *i.e.*, using only the equation (3).

By means of the above findings, the empirical rules about velocity can be explained easily. The rules for discussion will not be taken in the order presented.

Rule.—Presence of dipole moments enhances the velocity.

In terms of dipole orientation or Keesom forces (eq. 2), the rule is self-explanatory. But there are many other factors to be taken into consideration in this connection. We observe that the attractive forces are very short range forces (varying inversely as 7th power of the distance) and, so much so, that in an accurate analysis, the length and shape of molecules has to be taken into account, and interaction between parts of molecules considered, instead of molecules as a whole. Again the relative position and the nature of a dipole or dipoles in a molecule play a tremendous part in deciding the mode of molecular interaction. A dipole which is hidden in the rest of the molecule will not be as effective as that which is more open. The individual cases will be more fully discussed in the course of the analysis.

Associations.—Another phemomenon which must be taken into account, when considering effect of dipoles, is that of associations. It has been established from many evidences, *e.g.*, electron diffraction, dielectric polarisation, Raman and infra-red spectra that many so-called abnormal liquids like water, normal paraffin alcohols, carboxylic acids exhibit the tendency of their molecules to join, or associate in the form of clusters of two or more molecules. The molecules in any cluster are hard knit up among themselves, being directly under electric dipole forces, but are loosely attached to those outside, through only the residual forces. Now in sound vibrations in a liquid, we may approximately take any cluster to move as a whole, *i.e.*, not to have comparatively so much phase difference among its constituents as with respect to molecules outside. Hence the cohesive energy relevant in our case of sound velocities will be that between one group or association and other molecules or associations outside it. Now if associations are broken up while other things, *i.e.*, temperature, pressure, etc., remain the same, the great cohesive energies looked up in different associations will be released and molecules all round will be knit up more closely, due to the freed dipoles, with subsequent lowering of compressibility. Hence we have, taking the reverse, that, on forming associations, compressibilty will increase. This picture of association and its relation to compressibility is a rough one, but we do not yet know enough of liquid structure to be more definite in the circumstances. Another interpretation of associations is that the co-ordination

number is low, *i.e.*, the number of neighbours round a molecule in a liquid is less than what would be if random distribution of molecules existed. The presence of directed dipole forces gives an open structure to the liquid. When associations are broken, the cohesive energy rises, due to closer distribution of molecules.

The effect of association in increasing the compressibility is best seen in the case of water. The velocity goes on increasing and compresibility decreasing with temperature up to a certain limit. This is due to associations breaking with increase of temperature which affect the liquids in the manner opposite to that done by expansion and increase of intermolecular distance.

To discuss the rule of dipoles we take a few cases where the simple rule breaks down. Now nitrobenzene, chlorobenzene and aniline have dipole moments of 3.80, 1.56 and 1.55 Debye units, and yet their velocities are 1490, 1302 and 1662 m/s, and their compressibilities 37.6, 53.0 and 34.7 relative units. Considering the details mentioned above, this fact is not unexpected. The dipole NO_2 of nitrobenzene is well shielded by the big O atoms on one side and the benzene nucleus on the other and has very unfavourable condition for great intermolecular approach and formation of associations. Measurements of dielectric polarisation and infra-red spectroscopic data have well testified to this fact of the absence of any prominent associations. Due to large moment and absence of associations the compressibility is sufficiently low, and indeed much less than that of chlorobenzene, In chlorobenzene, the dipole is again inhibited from close intermolecular approach due to massive Cl atoms. Again, dielectric polarisation measurements reveal that the molecules form a so-called non-polar association, which means that the associating dipoles are not head-on (indeed they cannot do so from steric reasons) but interact in a way, so that their resultant dipole is nearly zero. With all these factors of unfavourable configuration of the dipole, low dipole moment, and the fact of formation of associations the compressibility is highest and velocity the least. Aniline has been found to be almost unassociated, from studies on infra-red spectra. Now the NH_2 dipole has H atoms which, being of small size, can approach very near to other molecules, thus causing intense intermolecular action. These two factors together contribute to the lowest value of compressibility of aniline.

Again acetone has a dipole moment of 2.7D and of water 1.5D, yet in the latter the compressibility is much lower and velocity much higher than in the former (compressibility 87 and velocity 1200 m/s). In acetone the dipole is shielded from one side, so that only the negative end O is outside on the surface of the molecule. In water the dipole is open on all sides. Again ether and acetone have higher dipole moments (2.7D and 1.50D) than the moment of chloroform (.8D), yet the compressibility of the last compound is the least. This is due to the dispersion forces among Cl atoms becoming important in magnitude. Alcohols and water have nearly the same dipole moment, yet there is great disparity in compressibilities and velocities.

Similarly numerous other cases can be quoted, stressing the need for not regarding the dipole action as represented only by the dipole moment as found from dielectric polarisation measurements.

Rule of viscosity :—Viscous liquids have higher velocities.

Viscosity is the temporary resistance offered to shearing of liquid molecules. Now it is evident that the greater the intermolecular field between molecules the more difficult it will be to displace them relative to one another. Hence we have, that greater the cohesive energy or less the compressibility, the greater the viscosity or less the fluidity, that latter being the reciprocal of viscosity. Of the numerous formulae set up for viscosity by Andrade, Frenkel, Raman and others, the general form is

$$\eta = Ae^{\frac{U}{KT}}$$

where A is a constant, K, T the usual symbols, and U an activation energy. This activation energy is the energy supposed to be parted to the molecules in order that they may overcome the potential barriers or be able to move from the pits of minimum potential energy. This U can be taken as a function of the cohesive energy, or inverse of compressibility. In fact Datta (6) (1943) has formulated the following :—

$$\eta = AT^{\frac{1}{2}}e^{\frac{b}{\chi}}$$

where η is viscosity and χ the compressibility.

The fact that viscosity and cohesion go together, and therefore viscosity and velocity, is also shown by their change with temperature. With rising temperature, the chaotic motion and the intermolecular distance increase. Due to the former, the frequency of relative position of molecules in the position of greatest cohesive interaction decreases, and due to the latter, the cohesive energy directly decreases by the increase of R in (3). Hence on these accounts viscosity and cohesive energy both decrease, the latter lowering the sound velocity.

Parthasarathy's rule about viscosity is covered by the above, but again, on analysing closer, we find that the rule is only approximate, like the rule of dipoles.

Now the fundamental difference between fluidity and compressibility is that the former is an irreversible or inelastic phenomenon of intermolecular action while the latter is an elastic one. The molecules displaced by shear have no tendency to come back, but the compressed molecules return to their original positions and configurations when the compressing pressure is removed. Again viscosity is concerned with the shearing of molecules, *i.e.*, movement of one molecule or molecular plane at right angles to the other, while the compressibility with the movement of molecules in their line of centres. Thus the viscosity, so to say, deals with the anisotropic behaviour and compressibility with symmetric

behaviour of molecules. The anisotropic molecules will have a viscosity that may not in cases be compatible with their value of cohesive energy or compressibility, and on the other hand the condition will be reversed when the molecules are more or less symmetric. Again viscosity and compressibility are very significantly related to association. While the compressibility increases with association, so does also viscosity, although by our approximate rule it should decrease. Due to association a bridge or mesh-like structure is produced which and the anistropy produced by it increase the shearing resistance and so the viscosity, while the cohesive energy is decreased due to decrease of immediate neighbours and other consideration given above.

EXAMPLE OF DEVIATION OF THE RULE

Carbon tatrachloride has more viscosity than chloroform, but the velocity and compressibility considerations are in the reverse order. Isobutyl and isopropyl alcohols have higher viscosities than the normal alcohols, thus not following Parthasarathy's rule. The velocity of water increases with increase of temperature in the ordinary range due to decrease of compressibility while the viscosity decreases. With increase of pressure to some range on water, its viscosity falls while velocity increases. Viscosity and compressibility behave oppositely for formation of hydrogen bonds. The viscosity increases with formation of hydrogen bonds, while sound velocity decreases and compressibility increases. The above is the example of water.

Rule.—Aromatic compounds have higher velocities than aliphatic compounds

The difference in these compounds which concerns our purpose lies in the following :—

Anisotropy of polarisability.—Aromatic compounds have their maximum polarisability axis at right angles to the plane of the molecule and aliphatic compounds have it along the molecular chain axis.

Two molecules in interaction will tend to set themselves in their maximum mutual force-field, *i.e.*, along their axis of maximum polarisability. The aromatic molecules along their axes of maximum polarisability will have their planes parallel. In this position, the atoms at corners of the planes will come in close proximity, and exert extra strong interaction due to individual dispersion or London forces. In the case of aliphatic compounds, the considerations are just the reverse. Not only is the cohesive energy less due to lower polarisability but also because end-to-end configuration brings in the least number of atoms in close proximity.

The difference in question between aromatic and aliphatic compounds may be shown from some kinds of experimental evidence, *e.g.*, heat of mixing of ethyl alcohol in benzene and carbon tetrachloride, or heptane; dielectric polari-

sation of alcohol in the above solvents, and the compressibility of alcohol-heptane and alcohol-benzene mixtures (Parshad, 1942; Wolf, 1937).

Rule.—Ortho compounds have highest velocity and para the least.

The polarisability and vector sum of dipole moments decrease in the order of ortho, meta to para, producing corresponding gradation in cohesive energy. Hence the rule on compressibilities and velocities. Now it must be borne in mind that the difference in question is small, and might be upset by any new factor, for example, by association, if any. In para compounds vector sum of zero dipole moments does not mean no dipole action. The dipoles are so far away, that they act nearly singly.

Rule.—Velocity increases as chain length of paraffin, aliphatic alcohols and ketones increases.

Chain length and alcohols.—Now the alcohols are associated liquids, and as has been shown the association decreases the cohesive energy. The increase of chain length would affect the intermolecular configuration in two ways :

(1) There would be more chain to chain aggregation. In fact the chain aggregation in long chain alcohols and paraffins is well known. Due to number of atoms increasing with increase of chain the end-to-end tendency will be overcome. The total dispersion forces between atoms in an increasing chain will also be increasing.

(2) The association of alcohol dipoles is in the direction of chain length. With increasing chain, therefore, the tendency of forming association is decreased. Badger and Bauer (1937) found that the association band of alcohols (in infra-red) decreases in intensity as chain length increases. This decrease or removal of associations leads to higher cohesional energy. In the case of paraffins the dispersion energy will increase with chain length, due simply to the increase in the number of atoms in a molecule.

In ketones, although the dipole moment may be thought to remain the same, the dispersion energy will increase with increase in the size of the molecule. And due to the shielding of the positive end of the dipole in ketones, the dispersion energy is quite appreciable relatively.

Rule.—Velocity decreases as chain length in ethers and esters increases.

(1) *Dipole moments.*—As chain length increases, the dipole moment decreases.

Methyl ether	...	dipole moment	1.29 D.
Ethyl ether	...	,, ,,	1.12 D.
Propyl ether	...	,, ,,	0.86 D.

The rule is self-explanatory.

Rule.—Unsaturated compounds have lower velocity.

The rule does not seem to be general. Ethyl bromide has the velocity and the compressibility of 892 m/s and 88.1×10^{-6} Ab units at 28°C while ethylene bromide has the respective values of 1014 and 44.7×10^{-6}. The same behaviour

is expected of ethyl chloride and ethylene chloride, but their values are not given in literature.

The following considerations support the rule :—

(1) *Double bonds and polarisability.*—A double bond has polarisability (Denbigh, 1940) slightly larger than a single bond, but considering that in any molecule the double bonds are formed at the cost of two single bonds, the total polarisability of a molecule with single bond is greater than that of a molecule of corresponding chemical class with double bonds.

(2) Due to residual valency forces, the unsaturated compounds form associated products, and this may tend to lower their velocity though we cannot push this conclusion far, as this association may have different grounds and other factors than those already considered.

(3) With removal of double bonds more atoms come into the molecule which can exert additional dispersion and other forces and so enhance cohesion, lower compressibility and increase velocity.

The following is against the rule :

Dipole action.—It has been shown by Smyth that the dipole moment of double bond between atoms of different elements is much more than twice the moment for a single bond, and similar is the case for a triple bond. For example the cyanide moment is eight times that of the single carbon-nitrogen bond, and double bonds between carbon and oxygen and between carbon and sulphur have moments slightly less than three times those of the single bond. The consideration seems to go against Parthasarthy's rule. But Parthasarthy studied the compounds $CHCl=CHCl$ and $CHCl_2.CHCl_2$; $CCl_2=CCl_2$, and $CHCl_2.CHCl_2$ and in these compounds the bonds are between similar atoms and so Smyth's conclusions are not strictly applicable here.

Rule.—Introduction of a heavier atom in the molecule decreases the velocity.

The rule seems just fortuitous as has been pointed out by Bergmann also. It seems to hold more with velocities than with compressibilities. As a matter of fact it seems just the reverse for compressibility.

In the table below R.H. denotes ' Rule held ' and R.N.H. denotes ' Rule not held.'

The table has been taken at length, due to many points involved. We note that Parthasarthy's rule about velocities is held in most of the cases, with exceptions here and there. What is more important to note is that the rule does not hold at all with regard to compressibilities except for the pair carbon-tetrachloride-chloroform.

Note.—Parthasarathy's rule about compressibility may be taken as meaning a decrease of compressibility where increase of velocity is indicated.

SUBSTITUTION OF A HALOGEN BY A HALOGEN

No.	Compound	Temp.	Velocity m/s		Compressiblity × 10 absolute units	
1	Butyl bromide	25.5	1016	R.H.	76.2	R.N.H.
	Butyl iodide	28.0	959		67.3	
2	Acetylene tetrachloride	28.0	1155	R.H	48.6	R.N.H.
	Acetylene tetrabromide	28.0	1007		33.3	
3	Chloroform	23.5	1001	R.H.	67.1	R N.H.
	Bromoform	24 0	929.8		40 0	
4	Methylene chloride	23.5	1064	R.H.	66 2	R.N.H,
	Methylene bromide	24.0	971 2		43 2	
	,, iodide	24	977.0	R.N.H.	31.5	R.N.H.
5	Ethylene chloride	23.0	1240.0	R.H.	51.8	R.N.H.
	,, bromide	24 0	1014		44.7	
6	Butyl bromide	28.0	1016	R.H.	76 2	R.N.H.
	,, iodide	28.0	959		67.3	
7	Chlorobenzene	23.0	1302	R.H.	53.6	R.N.H.
	bromobenzene	28 0	1134		52 0	

ADDITION OF HALOGENS

1	Monobromo-ethane	28	892	R.H	88.1	R.N.H
	Dibromoethane	34	1014		44.7	
	Tetrabromoethane	28	1007		33.3	
2	Methylene bromide	24	971	R.H.	43.2	R N H.
	Bromoform	23,5	929		40 0	
3	Chlorobenzene	23	1302	R.H.	53.6	R N H.
	Dichlorobenzene meta	28	1232		51.2	
	,, para	25	1246		49.7	
4	Chloroform	23 5	1001	R H.	67.1	R.H.
	Carbon tetrachloride	23 0	928.5		72 6	

The rule about velocity comes to be held for the reason that with increase of the mass of the halogen content the compressibility does not decrease so rapidly as the density increases, so that velocity on the whole decreases.

The following points may be offered relevant to the problem. As a heavier halogen atom is introduced, the following changes take place:—

(1) The dipole moment decreases. This consideration will decrease the velocity and increase the compressibility.

(2) The polarisability increases; the atomic number increases and so does the polarisability, as this depends upon the number and square of radii of different shells of electrons. This factor will tend to increase the cohesive energy.

(3) *Steric hinderance.*—As a bigger atom is substituted, it will be difficult for other molecules to approach it as near as before when the atom was smaller.

On this consideration, cohesive energy will decrease from chlorine to iodine. Actually it is the polarisability consideration which is the most outstanding and so compressibility falls when a heavier halogen is substituted for a lighter one, or when the halogen content is increased. We have seen in Eq. (1) and (3), how polarisability increases intermolecular cohesive energy.

The consideration of steric hinderance is hinted at by examining more closely the case of aliphatic and aromatic liquids. In aliphatic liquids, the decrea e in compressibility is relatively more than in aromatics and this may be significantly due to the different molecular structures of the two classes of liquids.

In aliphatic compounds, the question of steric hinderance is not expected to be much as the interaction is mainly end to end. But in aromatics, however, the consideration is different. We have seen before, that interaction in aromatic compounds is in the direction at right angles to the hexagonal planes and is on this account quite intense also. The presence of bigger atoms will debar the other C-H groups of the planes to come in the same close proximity as before and so interaction will be effectively decreased with the consequent increasing of compressibility from what it would be otherwise. The above explanation with regard to aliphatic and aromatic compounds throws additional light on the different modes of interaction in these compounds

Rule.—Velocity in isomers is different.

With regard to the consideration outlined in the beginning for establishing relations among cohesive energy, compressibility, molecular fields, etc., it is not difficult to see that different isomers should have different velocities and compressibilities. Isoalcohols have in general lower velocities and higher compressibilies than the normal alcohols as the dipole O-H, by coming in within the structure of the molecule, is unable to take as much an active part in interaction as when it is outside in normal alcohols. Of course in isomers of the optical kind, the molecules are identical as far as intermolecular action is concerned.

Other rules.

Besides the above rules of Parthasarthy, we introduce some further rules relating to compressibility and moleculer structure.

(1) *Rule.*—Increase of magnitude of diamagnetic susceptibility tends to increase sound velocity and decrease the compressibility.

Ortho substituted benzene have the greatest susceptibility and decrease in passing to meta and then, para, while velocity also in general varies in the same way.

The rule about diamagnetic susceptibility is also approximate and incidentally holds more for velocities than compressibilities.

(2) *Rule.*—Liquids having higher boiling points have higher velocities.

Examples are self-evident but still those of alcohols and hydrocarbons may be mentioned. Increasing chain length increases both the boiling point and velocity.

(3) *Rule.*—Liquids having greater heat of vaporisation have higher velocities.

(4) Increasing size of molecules show increasing velocity.

(5) The presence of many OH's in the molecules and situated distantly from each other, enhances sound velocity.

Example.—Velocity rises greatly and compressibility falls as we proceed from monohydric alcohols to polyhydric alcohols.

EXAMPLES

Liquid	Temp. C°	Velocity	Compressibility $\times 10^6$	Susceptibility.
(1) Methyl Alcohol	23·7	1130	98·9	—·65 (at −3·0°C)
Ethyl ,,	23·5	1207	87·3	—·01 (at −20°C)
Propyl ,,	24·0	1234	81·9	—·766
Butyl ,,	23·9	1315	71·5	—·743
(2) Methyl acetate	24·0	1211	73·5	—·509
Ethyl acetate	23·5	1187	79·0	—·581
(3) Chloroform	23·5	1001	67·1	—·488
Bromoform	24·0	929·8	40·0	—·316
Carbon tetrachloride	23·0	838·5	72·6	—·429
(4) Methylene chloride	23·5	1064	66·2	—·549
Methylene bromide	24·0	971·2	43·2	—·379
Methylene iodide	24·0	973·7	31·5	—·349
Bethylen chloride	23·0	1240	51·8	—·602
Ethylene bromide	24·0	1014	44·7	—·422
(5) Cyclonexanone	23·5	1411	50·8	—·648
Cyclohexanol	24·0	1622	40·2	—·727

DISCUSSION

Rule concerning diamagnetic susceptibility.

(1) Diamagnetic susceptibility and intermolecular energy.—Susceptibility is related to polarisability through the expression—

$4 - 1576P\alpha_2$

$$\frac{h^2 a}{8Mc^2\chi} = \Sigma_1^2,$$

where χ is susceptibility, a the polarisability, r the distance of the electron from the nucleus, the other symbols having their usual meanings. The expression for polarisability is approximate.

Kirkwood (1937) has given an empirical relation :

$$-\chi = \frac{1.e^2 a_0^{\frac{1}{2}} \sqrt{N\alpha}}{4mc^2},$$

a_0 is the value of 1 Bohr radius ;
and Buckingham (1937) gives the formula

$$\chi = \frac{-2e^2\alpha_0^2}{6mc^2} \cdot \nu_0 < r^2 >_0,$$

where α_0 is the polarisability of the ring of electrons ν_0 in number and of radius r_0.

London gives U the inter molecular energy between two molecule, as

$$U = -\frac{1}{R^6} \cdot \frac{6mc^2}{N_l} \cdot \frac{\alpha_k \alpha_p}{\frac{\alpha_k}{\chi_k} + \frac{\alpha_p}{\chi_p}};$$

k and p pertain to the two interacting molecules.
The above expression is for only a simple system of molecules having one strong frequency.

(2) Angus and Hill (1940).—They conclude by investigating the susceptibility of associating substances like benzoic acid in solvents like benzene and ethyl acetate that as association increases, susceptibility decreases. We have already seen how association increases the compressibility, and hence our rule of diamagnetic susceptibility. However Anantkrishnan and Varadachari (1944) criticise the conclusions of Angus and Hill. But as far as pure liquids are concerned decrease of association does seem to be reflected in increase of susceptibility. Thus Sibaiya (1935) finds that susceptibility of ice is considerably less than that of water, and Varadachari (1935) finds that susceptibility of water rises with temperature. Rao and Sriraman (1938) finds that molecular susceptibility of formic acid is 20.53 and that of the formate ion is 17.3. The two values should have been identical if formic acid molecule were monomeric and which we know to be mostly dimeric.

Rule.—Velocity increases with increase of heat of vaporisation and boiling point.

The exact mechanism of boiling, like that of melting, is yet obscure, but it can be roughly seen that before a liquid can boil, a molecule has to gain enough kinetic energy, so as to be able to overcome the force of cohesion that bind it to other molecules. The greater the cohesive energy, the greater the heat of

vaporisation. The boiling point will also rise with heat of vaporisation for boiling point is an indication of the heat of kinetic energy of a single molecule which has to counteract its cohesive energy. In fact according to Trouton's rule ML/T is constant for unassociated liquids where L = heat of vaporisation and T the boiling point and M is molecular weight. Lennard Jones (1939) gives the approximate formula

$$kT_b = \tfrac{3}{4}\phi_0,$$

where T_b is the boiling point and ϕ_0 the total attraction energy between a pair of molecules of the liquid. Now boiling is insensitive to the kind of molecular force of attraction holding the molecule before its escape, *viz.*, whether the molecule is associated or not. If it is not associated, it has to overcome the general sort of cohesion of other molecules upon it. If it is associated through a hydrogen bond or otherwise, it has to overcome mainly the attachment with its associated molecule or group. Due to these considerations, the relation between heat of vaporisation and compressibility is sometimes distorted.

Rule.—The size of molecule.

As the size of the molecule increases, there can be greater dispersion energy between the molecules leading to lower compressibility. It can be seen that as the size of the molecule increases, the state of any kind of molecule changes from the gas state to the liquid and then to the solid state. There is not much need here to labour the point further.

Rule.—Presence of many OH's in the molecule.

The greater the OH's in the molecule, the more will be the dipole interaction. The intensity of general cohesive interaction will be favoured by the placing of the OH's far from each other in the molecule. Then any steric hindrance of one OH for the other OH, in bringing other molecules for close interaction, decreases. By their acting independently, the OH's make the whole molecule active rather than some part of it, if the dipoles occur together. But we must note that in accordance with our previous treatment of the problem, it will be the viscosity that will increase at a more rapid rate than cohesion. The case in point is of polyhydric alcohols.

Similarly many other rules relating to surface tension, refractive index, dielectric constant, etc., may be formulated because all of them arise in general from factors causing cohesion.

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REFERENCES

Anant Krishnan and Varadachari, 1944, *Proc. Ind. Acad. Sc.* **20**, 128.

Angus and Hill, 1940, *Trans. Farad Soc.* **38**, 923.

Badger and Bauer., J., 1937, *Chem. Phys.* **5**, 839.

Buckingham, 1937, *Proc. Roy. Soc.* **94**, 160.

Datta, A. K., 1943, *Nature*, **1823**, 445.

Debye, 1921, *Phys. Zeits.* **22**, 302.

Denbigh, 1940, *Trans. Farad. Soc.* **56**, 936.

Keeson, 1916, *Proc. Amst.* **18**, 635.

Kirkwood, quoted in Buckingham (1937).

Lennard Jones, 1939, Interatomic forces, Indian Association for the Cultivation of Science, Calcutta

Parthasarthy, 1937, *Curr. Sci.*, **6**, 322.

Parshad, 1941, *Ind. J. Phys.*, **15**, 323; 1942, **16**, 1.

Rao and Sriraman, 1938, *J. Annamalai Univ.* **7**, 187.

Sibaya, 1935, *Curr. Sci.* **3**, 421, **4**, 41.

Smyth, Dielectric constant and molecular structure.

Varadachari, 1933, *Proc. Indi. Acad. Sci.*, **2**, 168.

Woll, 1937, *Trans Farad. Soc.* **33**, 179.